Nematic liquid crystals (NLCs) are anisotropic fluids that only exhibit uniaxial, apolar orientational order. In most liquid crystals, this order is temperature dependent, spontaneously arising at temperatures below the nematic-isotropic (N − I) phase transition temperature (TN−I); above this temperature the material exhibits no order (i.e., is isotropic). In many nematics, orientational order is particularly responsive to external influences, for example, electric and/or magnetic fields, mechanical strains, etc. [1–7]. This response is the primary reason that nematic liquid crystals are extensively used in information display applications like liquid crystal displays. External fields affect NLCs in two ways: they affect the degree of orientation order, or they reorient the axis of orientational order or fluctuations of positional order. A detailed calculation of the effects of molecular biaxiality found that this may also lead to anomalously large field effects for the N − I transition [14].

In this work, we report on unprecedented magnetic-field-induced shifts of the isotropic-nematic (I − N) phase transition temperature observed in liquid crystal dimers where two rigid linear mesogens are linked by flexible nonyl or heptyl chains [15]. The shapes of these molecules resemble nunchaku fighting sticks. The three compounds studied and their corresponding phase sequences are depicted in Fig. 1(a). The first compound, 1′′,7′′-bis(4-cyanobiphenyl-4′-yl)nonane (CB9CB), was synthesized as described in Ref. [16]. The synthesis of the second and third dimers, 1,1,1-di(2′′,3′′-difluoro-4-pentyl[1,1′′;4′,1′′]terphen-1′′-yl)nonane (DTC5C9) and 1,1,1-di(2′′,3′′-difluoro-4-pentyl[1,1′′;4′,1′′]terphen-1′′-yl)heptane (DTC5C7), is described in Ref. [17]. The three compounds exhibit the recently discovered twist-bend nematic (NTB) liquid crystal phase, in which the director follows an ambidextrous conical helix with a remarkably short pitch in the 10 nm range [18,19]. Thus, the NTB phase can be considered as a nanoscale pseudolayered structure [20–22], which explains the smectic-like textures [20–24] and viscoelastic properties [25] of the NTB phase, despite the lack of a density modulation characteristic of a true smectic [18,24,26].
The temperature dependencies (on cooling) of the effective birefringence $\Delta n$ and the dependence of $T_{N-I}$ on magnetic fields are shown in Fig. 2. At the zero field, the discontinuity in birefringence at $T_{N-I}$ is plainly visible in CB9CB; it is smaller for the two other compounds. Under magnetic fields the birefringence is larger in the entire nematic range, although the increment at the $N-I$ transition appears smoother. The field-induced increase of the birefringence may indicate quenching of the fluctuations and/or an increased aspect ratio of the molecules. The data shown correspond to cooling from above $T_{N-I}$. The same behavior is observed in heating, although the transition temperature is observed to be approximately 1 °C higher.

In a 22 T magnetic field, $T_{N-I}$ increases dramatically, by at least 8 °C in all three compounds and by almost 15 °C for DTC5C7. We know of no other example of such a large magnetic field effect on a nematic-isotropic transition for a thermotropic liquid crystal. Indeed, this effect is more than 300 times larger than what has been reported previously for rod-shaped thermotropic compounds. We also performed measurements at several weaker magnetic fields. As can be seen on the right-hand side of Fig. 2, the transition temperature shift $\Delta T_{N-I}$ increases almost proportionally to $B$, and is not proportional to $B^2$, as was found for other thermotropic materials [11,13].

When the samples are held at temperatures just above the zero-field $T_{N-I}$ and are then subjected to an increasing magnetic field, the field induces the nematic phase. If the field is subsequently reduced to 0, the isotropic phase returns to a field just slightly lower than that at which the nematic phase was induced. No discontinuity in birefringence (as in Fig. 2) is observed in this field-induced transition (see Fig. 3), due to the fact that the field was continuously changing (typically at 5 T/min) during the measurements. At temperatures further away from the zero-field $T_{N-I}$ the threshold field where the $I-N$ transition is induced increases, as seen in Figs. 3(a)–(3c). In Fig. 3(d) we compare $\Delta n(B)$ of the three studied materials at 5 K above the zero-field $T_{N-I}$. The compound CB9CB shows a more rapid onset of birefringence with an applied magnetic field compared to the other compounds.

Magnetic fields interact with liquid crystals mainly via the molecules’ aromatic ring moieties. The free energy contribution due to an applied field is minimized when the ring plane normals are perpendicular to the field. In fully rigid molecules this occurs with the molecular long axis aligning parallel to the field. The most profound effect of this interaction is the reorientation of rigid rod-shaped molecules along the external field. Additionally, when the director is already aligned along the field, a magnetic field can couple to the magnitude of the orientational order, which can be described by Landau–de Gennes [31] or Maier-Saupe [32] theories. Both theories predict that a magnetic field leads
induces a $\Delta T_{N-I}$ that is linear in $\Delta \chi_0$, quadratic in $B$ in contrast to our observations shown in Figs. 2(a)–2(c). They show that in our dimers the $N - I$ transition temperature increases roughly linearly with the magnetic field. A possible linear contribution to the phase shift related to field-induced quenching has been discussed by Dhara and Madhusudana [33]. However, this effect is even smaller than the field-enhanced order that is contained in Landau–de Gennes theory and as such is not a candidate for explaining the linear dependence we observe.

Moreover, Landau and de Gennes predict that $T_{N-I}$ also depends inversely on the latent heat of the $N - I$ transition. However, in order for this mechanism to explain the magnitude of $\Delta T_{N-I}$ observed, these compounds would require either (i) diamagnetic anisotropy hundreds of times larger than in typical rod-shaped thermotropic compounds (which may be ruled out due to their similar cores based upon aromatic rings) or (ii) $N - I$ latent heat thousands of times smaller, which is also not the case [34].

Hence we conclude that field enhancement of nematic order, as predicted by the Landau–de Gennes theory for simple rodlike mesogens, cannot explain the observed values for $\Delta T_{N-I}$. Lastly, the three compounds we have studied show no indications of other varieties of ordering (or fluctuations thereof), such as positional clustering [17,23,25] or biaxiality, which have been proposed to explain otherwise inexplicably large $\Delta T_{N-I}$ [12,13].

Most theories relating molecular morphology to the onset of the $N - I$ transition derive from Onsager [35]; however, approaches based only on excluded volume

FIG. 2. Temperature dependence of effective birefringence and magnetic field dependence of the $I - N$ transition temperatures. Left: Temperature dependence of birefringence at $B = 0$ (blue) and $B = 22$ T (red) for CB9CB (a), DTC5C9 (b), and DTC5C7 (c) measured on cooling at a $2^\circ C/\min$ rate. Right: $T_{N-I}$ as a function of the magnetic field $B$ for CB9CB (a'), DTC5C9 (b'), and DTC5C7 (c'). Data with arrows up arrow, down arrow, right arrow, left arrow are taken on heating, cooling, increasing fields, and decreasing fields, respectively.
effects are athermal and cannot provide insight to transition temperatures. Onsager-type models have been hybridized \cite{36,37} to contain the effects of both anisotropic, rigid shapes and anisotropic inter-molecular interactions (treated via the mean field). While these models do not aspire to describe the more complex shaped mesogens in the present work, they do indicate that $T_{N-I}$ increases strongly with mesogens’ aspect ratio (length/diameter). This fits broadly with experimental results for linear rigid aromatic ring systems \cite{36–38}.

Owing to the odd-numbered methylene groups in the linking group, the average molecular shape of the materials we studied is bent (i.e., nonzero $\beta_0$ as shown in Fig. 4). However, due to the inherent flexibility of the alkyl bridge between the two arms, the shape can be relatively easily altered. A decrease of the bend angle effectively increases the aspect ratio of the dimer, which should produce a significant increase of $T_{N-I}$; this is predicted by multiple models \cite{39–41}. For example, Ref. \cite{39} estimates that, for dimers linked by a nonyl chain, a reduction of only 3° leads to a 4% increase in $T_{N-I}$ (in absolute temperature), which is larger than the shift we report. This suggests that a magnetic-field-induced straightening of the molecules is responsible for the magnetically induced large shift of $T_{N-I}$ recorded in our experiments in high fields. The role of the molecular shape on $T_{N-I}$ is also evidenced in the anomalously large “odd-even” effects observed in the $T_{N-I}$ transition temperature. For an even number of methylene linkages (that promote a straight or linear molecular conformation) the phase transition temperatures for % 1”,7”-bis (4-cyanobiphenyl-4’-yl)alkane % (CBnCB) molecules were found to be 50°C higher than for the odd-numbered homologs that possess a more bent shape \cite{42,43}.

Our hypothesis is therefore that the effect of a large field is that it straightens out the dimers on average, aligning the two rigid arms more parallel to a common axis than would be found in the zero field. This mechanism is illustrated in Fig. 4.

We note that the effect of the shape, i.e., the odd-even effect, is

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Effective birefringence measurements as the function of magnetic field $B$: (a) CB9CB at 130 and 140°C; (b) DTC5C9 at 169 and 172°C; and (c) DTC5C7 at 165 and 169°C. The arrows $\uparrow$ ($\downarrow$) show measurements at the field ramping up (down) at a 5°C/ min rate. (d) Comparison of the three materials at 5°C above the zero-field $T_{N-I}$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4.png}
\caption{Illustration of the magnetic-field-induced decrease of the molecular bend, and its consequence of the shift of $T_{N-I}$.}
\end{figure}
decreasing toward higher homologs, which is corroborated by our observation (see Fig. 2) that the field-induced phase shift is smaller for DTC5C9 than for DTC5C7.

Here, we note that the magnetic-field-induced downward shift of the \( N - N_{TB} \) transition of two other dimers CB7CB and KA(0.2) has already been reported by Challa et al. [30]. This seems to confirm our conjecture about the straightening and KA(0.2) has already been reported by Challa et al. [30].

To summarize, we have observed a large magnetic-field-induced elevation in the nematic to isotropic phase transition temperature in various thermotropic liquid crystal dimers containing an odd number of methylene groups in the linkage between the two terminal mesogenic moieties. We attribute this unprecedented shift to a field-induced straightening in the average conformation of the dimers. The impact of an electromagnetic field at the molecular level on the ordering of an ensemble of mesogens has not (to our knowledge) been previously reported.

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